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Thermochemistry of halogenobenzoic acids as an access to PC-SAFT solubility modeling

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ABSTRACT

Absolute vapor pressures and molar sublimation enthalpies of 2-, 3-, and 4-monohalogenobenzoic acids (halogen = fluorine and iodine) were derived from transpiration measurements. Molar enthalpies of fusion were measured by DSC. Thermochemical data available in the literature were collected, evaluated, and combined with own experimental results in order to recommend sets of sublimation and fusion enthalpies. Further, the recommended data were used to estimate PC-SAFT pure-component parameters. These parameters were applied to predict the solubility of the monohalogenobenzoic acids in water at 298.15 K, yielding satisfying prediction results. This approach proved the capability of PC-SAFT to predict solid–liquid phase equilibria if precise data on sublimation pressures and fusion properties is available.

1. Introduction

Halogenobenzoic acids are known to be toxic to biological environments, and these substances are slowly biodegraded [1]. However, several organisms are able to metabolize (oxidize, dehalogenate, mineralize) monohalogenobenzoates [2–5], meaning that these organisms can grow using halogenobenzoic acids as carbon source. Comparative metabolism of different halogenobenzoic acids is thus important for general understanding of metabolic pathways involving halogenobenzoic acids [6]. The reliability of modeling metabolic processes depends on the quality of experimental thermochemical input data. Such data include formation properties such as Gibbs energy of formation, which data are accessible by combination of vapor pressure measurements with calorimetric studies [7]. In recent works, these thermochemical properties were evaluated for chlorobenzoic acids and bromobenzoic acids [8,9]. Available experimental data on fluorobenzoic acids and iodobenzoic acids already exist, but are still scarce [10–16]. Thus, additional experimental studies are desired that allow recommending a precise set of data. Mutually consistent results can be obtained by independently measured data (using different techniques), which can then be used as a basis for analysis and evaluation of available data.

Aqueous solubility of biomolecules and chemicals is an important property that is required for crystallization processes. Further, aqueous solubility has to be known for analyzing metabolic processes as solubility presents the maximum amount of a compound that is present in a liquid aqueous environment. Benzoic acid derivatives are known to be sparingly soluble in water. Data on aqueous solubility are scarcely available in the literature [17], and often given at room temperature only. Thus, a thermodynamic model is desired which is able to predict solubility. State-of-the-art g^E models (e.g. NRTL, UNIQUAC) require typically 3–5 binary parameters in order to calculate phase equilibria such as solubility in water. The drawback of such g^E-models is that they do not allow solubility predictions as binary parameters are required. Even

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